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<b>(21) International Application Number:</b> PCT/NO96/00269 <b>(22) International Filing Date:</b> 15 November 1996 (15.11.96) <b>(30) Priority Data:</b> 954674 20 November 1995 (20.11.95) NO <b>(71) Applicant (for all designated States except US):</b> NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TILOKAVICHAI, Pytoon [TH/TH]; 9/158 Mooban Somlej Vile, Klongmahasawat, Bangkok, TH-Nontaburi 11130 (TH). CONRADSEN, Arne [NO/SG]; 23 Leonie Hill, 07-01 Leonie Gardens, Singapore 239224 (SG). GUSTAVSEN, Per, Fredrik [NO/NO]; Bergsbygdav. 436, N-3945 Eidanger (NO). <b>(74) Agent:</b> SUNDNES, Arne; Norsk Hydro ASA, N-0240 Oslo (NO).	<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> METHOD FOR COLOURING OF FERTILIZER BLENDS AND PRODUCTS THEREOF  <b>(57) Abstract</b>  The invention relates to fertilizer blends having homogeneous appearance and where the particles of the fertilizer blends have been coated with 0.1-1 wt.% pigments and a method for homogeneously colouring such blends comprising coating the fertilizer particles with 0.1-1 wt.% pigments comprising white silica pigments having a particle size of 0.01-1 $\mu\text{m}$ and a surface area of 100-550 $\text{m}^2/\text{gram}$ and at least one pigment having particle size of 0.1-100 $\mu\text{m}$ and a surface area of 10-100 $\text{m}^2/\text{gram}$ and 0.0-0.5 wt.% oil. Optionally the coating may contain 5-20 % of the amount of oil of an oil-soluble polymer or resin. The ratio of white silica pigment : pigments having particles size of 0.1-100 $\mu\text{m}$ can be 1:3 to 3:1.		

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## **"Method for colouring of fertilizer blends and products thereof"**

The present invention relates to a method for colouring of fertilizer blends and fertilizer blends coloured according to said method.

Colouring of fertilizers is well known in the art. Various types of pigments like black microsilica, black-, yellow- and red iron oxides etc. have been used to give the fertilizer particles the desired colour in order to distinguish one fertilizer over other types of fertilizers or fertilizers from other manufacturers. The pigments can be applied alone or together with oil and thereby secure an even distribution of the pigment on the fertilizer particles.

Colouring of fertilizer blends have also been tried out, but with very little success. There are several reasons for the problems experienced in colouring blends. Firstly, the blends consist of different types of fertilizers and these may have different particle size making the large particle giving a dominant look if they have a colour different from the other types of particles. The main reason however, is that the pigments, with or without oil, do have varying ability to adhere to the particles of the various types of fertilizer which the blend consists of. Thus a blend which originally seemed to have a homogeneous colour, soon became unhomogeneous in colour when exposed to normal handling of the blend. Such handling include the blending operation itself, transportation by conveyer belts, loading and unloading operations etc.

The main object of the invention was to arrive at a method for giving the fertilizer blends a homogeneous appearance with regard to colour.

Another object was to apply colourants/coating systems which could mask the colours of the components and thereby improve the visual appearance of the mechanical mixture of fertilizer components.

A further object was to arrive at fertilizer blend products being homogeneous in colour regardless of the original colours of the various components of the blends.

A thorough evaluation of different ways of colouring fertilizers revealed that water-soluble agents for colouring were not applicable for surface colouring. Surface colouring by means of oil-soluble agents were also investigated. Though such treatment works well for colouring single components, they were found to be insufficient for blends due to different absorbing abilities of the component and low hiding power of the organic layer.

Based on the results of the preliminary investigations, it was decided to test the effects of applying pigments (normally oxides), alone or together with oil, or with oil containing polymers. The oil used during these experiments was white oil, but other types of oils commonly used in fertilizer coatings would also be applicable. Useful types of such oils comprise any of several derivatives of paraffinic hydrocarbons having moderate viscosity, low volatility and a high flash point. Vegetable oils such as corn oil, canola oil, sunflower oil, soya oil, linseed oil or mixtures thereof are also applicable. Refined mineral oils will also be applicable, but are not recommended from an environmental point of view.

Polymers can be added in order to increase adherence, but primarily for reducing dust formation during handling of the fertilizers. Suitable polymers would be polyisobutylene, (PIB), resins and wax. Examples of applicable polymers for the

present purpose comprise synthetic resins having high molecular weight, such as cumarone-indene, pentaerythritol ester of rosin, esterified natural resins like rosin, phenolformaldehyde resins, furfuryl alcohol resins, polyester resins and polyurethane resins. Examples of some useful natural resins are rosin, congo, balsam and damar.

The following systems were investigated:

PIGMENT	OIL	POLYMER
Red iron oxide	White oil	PIB, Resin, WAX
Yellow iron oxide		
Grey silica		
Black silica		
White silica (SYLLOID)		
White precipitated silica		
Laca Verde 778 (PROQUIMAC)		
Laca Verde 889 (PROQUIMAC)		
Laca Indigo Carmin 10 (PROQUIMAC)		

The "PROQUIMAC" pigments are metal oxides.

The white silica pigments used should have a very small particle size, i.e. about 0.01-1 $\mu$ m and have a large surface area, about 100-550 m<sup>2</sup>/gram. Such silica quality can be obtained by using precipitated silica, but other production methods can be used for obtaining similar qualities. Examples of commercially available silica of the above defined quality are sold under the trademarks "Sylloid", (Grace), "Sipernat" and "Aerosil" (Degussa) and "Perkasil" (Oriental Silica), and "Silcasil" (Bayer). These pigments were applied on fertilizer blends alone or together with oil or together with oil and polymer.

During the performed experiments it was surprisingly found that a combination of said white silica pigments with other types of pigments produced even coatings on all types of fertilizer components and gave the blends a homogeneous appearance. There might be several explanations to the observed effect, but the fact that the high specific area silicas can absorb large quantities of both water and oil without getting wet and sticky might be an explanation of the successful results. With its small particle size and large surface area the white silica will adhere strongly to the surface of all the fertilizer particles and create a stable and equal base for the second pigment. Such silica has also good anticaking effect.

The ratios between white silica and the other pigments could be varied within wide ranges. Ratios of about 1:1 seemed to be optimal, but this ratio could be varied between 1:3 to 3:1. The total amount of pigment powder applied should be in the range 0.3-1%. Preferred amounts would be 0.2-0.8 weight%. Oil could be added in amounts of up to 0.5% without making the final product sticky. Preferred amounts of oil were found to be 0.05-0.3%. When pigments only were applied to the blends, homogeneous colour appearance was achieved, but the blend products were somewhat dusty. In most cases it will be an advantage to also apply oil together with the pigments.

Addition of polymer to the coating mixture was primarily made for reducing dust formation. The polymer will make the coating more viscous and the amount used must be decided in view of that. Too much polymer will make the coating process difficult and can also make the final product somewhat sticky. Thus the amounts of polymer will mainly be governed by practical measures, useful amounts were found to be about 10% of the amount of oil used. 5-20% polymer of the amount of oil used will be an applicable range. The polymer/resin should be oil-soluble.

The scope and special features of the invention are as defined by the attached claims.

The invention will now be further explained by the following examples:

### **Example 1**

This example describes a series of experiments for colouring of blends consisting of monoammonium phosphate (MAP), urea and potassium chloride (KCl). These components are used to make up a blend of NPK 14-10-30 (30% urea, 20% MAP and 50% KCl). The temperature of the blends during the coating process was kept at 22-25°C. The amounts of pigments were varied between 0.2-0.8 weight% of the total weight of the blends. White oil was mixed in amounts of about 0.1 weight% of the total weight of the blends.

The white silica (WS) pigments used had a particle size of 0.01-1  $\mu\text{m}$  and a surface area of 100-550  $\text{m}^2/\text{gram}$ . The black silica (BS) and grey silica had a particle size of about 0.1-40  $\mu\text{m}$  and a surface area of 20-70  $\text{m}^2/\text{gram}$ .

The results of the experiments are shown in table I.

**Table I**

<b>Pigment</b>	<b>Amount of pigment %</b>	<b>Oil %</b>	<b>Homogeneity</b>
Black silica (BS)	0.30-0.40	0.10	Not satisfactory
Grey silica	0.30-0.60	0.10	Not satisfactory
Yellow Iron Oxide	0.30-0.50	0.10	Not satisfactory
Laca Verde 889	0.20-0.40	0.10	Not satisfactory
Laca Verde Indigo Carmin 10	0.20-0.40	0.10	Not satisfactory
Red Iron Oxide (RO)	0.20-0.40	0.10	Not satisfactory
White silica (WS) + RO 2:3	0.50	0.10	Good
RO+WS 1:1	0.40	0.10	Good
RO+WS 1.1	0.50	0.10	Good/excellent
RO+WS 1.1	0.50	0.10	Excellent
BS+WS 1.3	0.50	0.10	Not satisfactory
BS+WS 3:2	0.50	0.10	Good
BS+WS 1:1	0.50	0.10	Good
BS+WS 1.1	0.70	0.10	Excellent
BS+WS 1.1	0.80	0.20	Excellent
BS+WS (1:1)	0.70	0.15	Excellent

From the above table I it can be seen that the combination of white silica and other pigments gave a homogeneous colour appearance of the blends. Relatively large amounts of white silica seemed to have negative effect on the homogeneous appearance. When only one type of pigment was used, such as iron oxides or black silica only, the results were not satisfactory.

The caking properties of these blends were also checked by comparing uncoated NPK 14-10-30 blends with the same type of fertilizer coated according to the invention and coating with one pigment only. This test gave the following results:



Treatment	Caking Index
Uncoated NPK 14-10-30 blends	1100
0.3%BS + 0.3%WS + 0.1% oil	380
Red iron oxide 0.4% + 0.1% oil	406

### Example 2

This example shows the effect of applying a resin/polymer together with the oil in order to reduce dust formation. The oil used was white oil and the polymers, resin I and resin II were respectively polyisobutylene and polyethylene. The dust was measured according to a standard dust test comprising fluidizing the fertilizer particles with air, whereby the dust is carried upward by the airstream having a velocity of  $0.56\text{ms}^{-1}$  and collected in a filter.

The results of these experiments which were performed on NPK 14-10-30 blends are shown in table II.

**Table II**

Coating treatment	Dust, mg/kg
Laca Verde 0.3% + 0.1% oil	2100
0.25%WS + 0.25%BS + 0.1% oil	1300
0.25%WS + 0.25%BS + 0.1% with 10% resin I	950
0.25%WS + 0.25%BS + 0.1% oil with 10% resin II	900
0.3%WS + 0.3%BS + 0.1% oil	1200
0.3%WS + 0.3%BS + 0.25% oil	800
0.4%WS + 0.4%BS + 0.1% oil	1500

This example shows that addition of polymers to the oil has positive effect on the reduction of dust formation. The viscosity of the oil-polymer mixture must, however, not be too high because that will make the fertilizer sticky and deteriorate the homogeneity of the pigment colouring.

By the present invention the inventors have managed to arrive at a method for making fertilizer blends homogeneous in colour appearance and produce blend products being homogeneous in colour. The colouring or coating process can be performed in one or two steps, i.e. the fertilizer blends can first be coated with white silica and then with another pigment or all the pigments in question can be supplied onto the fertilizer blend in one step only. If one of the components of the fertilizer initially has an outstanding colour, this colour can be masked by applying the method according to the invention.

Claims

1. Method for homogeneously colouring fertilizer blends comprising coating the fertilizer particles with 0.1-1 weight% pigments comprising white silica pigments having a particle size of 0.01-1 $\mu$ m and a surface area of 100-550 m<sup>2</sup>/gram and at least one pigment having particle size of 0.1-100 $\mu$ m and a surface area of 10-100 m<sup>2</sup>/gram and 0.0-0.5 weight% oil.
2. Method according to claim 1  
characterized in that  
a coating containing 5-20% of the amount of oil of an oil-soluble polymer or resin is applied.
3. Method according to claim 1,  
characterized in that  
there is applied a ratio of white silica pigment : pigments having particle size of 0.1-100  $\mu$ m of 1:3 to 3:1.
4. Method according to claim 1  
characterized in that  
the fertilizer blend particles are coated with 0.05-0.3 weight% white oil, 0.2-0.8 weight% pigment in a ratio white silica : black silica of about 1:1.
5. Method according to claim 1,  
characterized in that  
the fertilizer blend particles are coated in two steps, the first comprising coating the particles with oil and white silica and the second comprising coating the fertilizer particles with oil and pigments having particle size of 0.1-100  $\mu$ m.

6. Method according to claim 1,  
characterized in that  
the fertilizer blend particles are coated with oil containing 5-15% of the  
amount of oil of an oil-soluble polymer or resin and white silica and at least  
one pigment having particle size of 0.1-100  $\mu\text{m}$
7. Fertilizer blends having homogeneous appearance and where the particles of  
the fertilizer blends have been coated with 0.1-1 weight% pigments com-  
prising white silica having particle size of 0.01-1  $\mu\text{m}$  and a surface area of  
100-550  $\text{m}^2/\text{gram}$  and at least one pigment having particle size of 0.1-100  $\mu\text{m}$   
and 0.0-0.5 weight% oil, and where said coating may comprise 5-20% of the  
amount of oil of an oil soluble polymer or resin.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 96/00269

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C03G 3/00, C05G 3/10, B01J 2/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C05G, C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3997636 A (FRANK WILLIAM BENNETT), 14 December 1976 (14.12.76), column 3, line 13 - line 28, claims 1,8 --	1-7
A	Derwent's abstract, No 77-15379Y/09, week 7709, ABSTRACT OF JP, 52006644 (CHISSO CORP), 19 January 1977 (19.01.77) --	1-6
A	Derwent's abstract, No 92- 30443/04, week 9204, ABSTRACT OF JP, 3278830 (AGENCY OF IND SCI TECH), 10 December 1991 (10.12.91) --	1-6



Further documents are listed in the continuation of Box C.



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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5290962 A (DALE M. OZDOBA ET AL), 1 March 1994 (01.03.94), abstract, example 3  -- -----	1-6

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

03/02/97

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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